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# Synthesis and electrochemistry of Co(III) and Co(I) complexes having C<sub>5</sub>Me<sub>5</sub> auxiliary

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## Abstract

The synthesis and electrochemistry of half-sandwich type of Co(III) complexes [(C<sub>5</sub>Me<sub>5</sub>)Co(bidentate)(CH<sub>3</sub>CN)](BF<sub>4</sub>)<sub>2</sub> {bidentate=dppe (1,2-bis(diphenylphosphino)ethane), dppp (1,3-bis(diphenylphosphino)propane), bpy (2,2'-bipyridine), en (ethylenediamine)} are reported. Cyclic voltammograms of [(C<sub>5</sub>Me<sub>5</sub>)Co(bidentate)(CH<sub>3</sub>CN)](BF<sub>4</sub>)<sub>2</sub> in CH<sub>3</sub>CN showed two redox couples assignable to Co(II)/Co(III) and Co(I)/Co(II). The Co(I) complex having C<sub>5</sub>Me<sub>5</sub> and dppe was also prepared. Two redox couples of this Co(I) complex, (C<sub>5</sub>Me<sub>5</sub>)Co(dppe), in CH<sub>3</sub>CN coincided with those of [(C<sub>5</sub>Me<sub>5</sub>)Co(dppe)(CH<sub>3</sub>CN)](BF<sub>4</sub>)<sub>2</sub> in spite of the structural change around the metal center.

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**Keywords:** Cobalt; Pentamethylcyclopentadienyl; Bidentate ligand; Cyclic voltammograms

## 1. Introduction

The use of fossil fuel as major energy source has risen up the amount of carbon dioxide in the atmosphere and brought several environmental problems like greenhouse effect or global warming. One possible solution is to use hydrogen as an energy source, which affords only water as its waste. Although hydrogen is at present mainly produced from hydrocarbons, it needs to be produced from water by use of natural energy for true environmental cleanness. In this context, photochemical splitting of water to hydrogen and oxygen has widely been studied [1]. On the other hand, natural photosynthesis produce oxygen and highly reducing NADPH by use of low-energy visible light with an elaborate set of molecular machinery. By mimicking photosynthesis at molecular level, we would get useful knowledge for artificial use of solar energy.

To achieve water splitting based on photosynthetic models, it is important to find suitable catalysts for reduction of H<sup>+</sup>. There is a large amount of examples of Pt catalyst for the H<sub>2</sub> production [2] but Pt is a rare metal and resource is limited, so that it is desirable to find catalysts based on cheaper elements like first-row transition metals. One of the candidates is Co; the

strong basicity of low-valent cobalt complexes [3–9] is beneficial for reduction of H<sup>+</sup>, and indeed researches for the H<sub>2</sub> production utilizing Co complexes have been reported in the last two decades [10–12]. Spiro et al. examined hydrogen production from H<sub>2</sub>O catalyzed by a Co porphyrin complex with a view toward an efficient electrocatalyst [10]. Koelle et al. described electrochemical reduction of H<sup>+</sup> by use of (C<sub>5</sub>H<sub>5</sub>)Co(PR<sub>3</sub>)<sub>2</sub> and spectroscopic determinations of hydride complexes as intermediates in the reaction [11,12]. In the latter study, the electrochemistry of reduction of H<sup>+</sup> was examined, whereas no structural information of the metal core at different oxidation states was reported.

In this report, we describe synthesis of a series of Co(III) complexes [(C<sub>5</sub>Me<sub>5</sub>)Co(bidentate)(CH<sub>3</sub>CN)](BF<sub>4</sub>)<sub>2</sub> and demonstrate a reversible interconversion between Co(III) and Co(I) in CH<sub>3</sub>CN solution by using cyclic voltammetry and X-ray crystallography. The structures of both oxidation states were elucidated and compared.

## 2. Materials and methods

### 2.1. General

All reactions and the manipulations of air-sensitive compounds were performed under an inert atmosphere using standard Schlenk and glovebox techniques. Solvents were dried, degassed, and distilled from sodium/

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Table 1

Summary of Crystallographic data for [(C<sub>5</sub>Me<sub>5</sub>)Co(dppe)(CH<sub>3</sub>CN)](BF<sub>4</sub>)<sub>2</sub> (**2**), [(C<sub>5</sub>Me<sub>5</sub>)Co(dppp)](BF<sub>4</sub>)<sub>2</sub> (**3**), [(C<sub>5</sub>Me<sub>5</sub>)Co(bpy)(CH<sub>3</sub>CN)](BF<sub>4</sub>)<sub>2</sub> (**4**), [(C<sub>5</sub>Me<sub>5</sub>)Co(en)(CH<sub>3</sub>CN)](BF<sub>4</sub>)<sub>2</sub> (**5**), [(C<sub>5</sub>Me<sub>5</sub>)Co(dppe)] (**6**)

|  | (2)   | (3)   | (4)   | (5)  | (6)  |
|--|---|---|---|--|--|
| Formula  | C <sub>38</sub> H <sub>42</sub> NCoP <sub>2</sub> B <sub>2</sub> F <sub>8</sub> | C <sub>41</sub> H <sub>47</sub> N <sub>2</sub> CoP <sub>2</sub> B <sub>2</sub> F <sub>8</sub> | C <sub>24</sub> H <sub>29</sub> N <sub>4</sub> Co B <sub>2</sub> F <sub>8</sub> | C <sub>14</sub> H <sub>26</sub> N <sub>3</sub> CoB <sub>2</sub> F <sub>8</sub> | C <sub>36</sub> H <sub>39</sub> CoP <sub>2</sub> |
| Formula weight                                       | 807.24  | 862.32  | 606.06  | 468.92   | 592.58   |
| Crystal system                                       | Monoclinic  | Monoclinic  | Monoclinic  | Monoclinic   | Monoclinic                                       |
| Space group  | <i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)                                     | <i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)   | <i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)                                     | <i>Cc</i> (No. 9)  | <i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)      |
| <i>a</i> /Å  | 12.342 (7)  | 18.982 (6)  | 14.017 (5)  | 10.8800 (11)   | 8.349 (4)  |
| <i>b</i> /Å  | 23.124 (12)   | 11.281 (3)  | 20.581 (6)  | 13.1745 (14)   | 18.687 (9)                                       |
| <i>c</i> /Å  | 13.038 (8)  | 19.061 (5)  | 19.457 (6)  | 14.546 (2)   | 19.626 (10)                                      |
| $\alpha$ /°  |   |   |   |  |  |
| $\beta$ /°   | 92.953 (8)  | 92.999 (4)  | 90.846 (5)  | 95.450 (8)   | 90.488 (6)                                       |
| $\gamma$ /°  |   |   |   |  |  |
| <i>V</i> /Å <sup>3</sup>                             | 3716 (4)  | 4076 (2)  | 5612 (3)  | 2075.6 (4)   | 3062 (3)   |
| <i>Z</i>   | 4   | 4   | 8   | 4  | 4  |
| $\mu$ /cm <sup>-1</sup>                              | 6.18  | 5.688   | 6.855   | 9.005  | 6.884  |
| No. reflections measured                             | 29,289  | 31,397  | 43,970  | 7678   | 21,976   |
| Unique reflections                                   | 8479  | 9299  | 12,767  | 4255   | 6625   |
| GOF on <i>F</i> <sup>2</sup>                         | 1.000   | 1.002   | 1.134   | 0.843  | 1.000  |
| <i>R</i> 1 ( <i>I</i> > 2 ( $\sigma$ )) <sup>a</sup> | 0.072   | 0.067   | 0.078   | 0.041  | 0.059  |
| <i>wR</i> 2 (all data) <sup>b</sup>                  | 0.212   | 0.234   | 0.187   | 0.111  | 0.219  |

$$R\ 1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad {}^b wR2 = [\sum w (|F_o| - |F_c|)^2 / \sum w (F_o^2)]^{1/2}.$$

benzophenone ketyl (diethyl ether, THF) or from CaH<sub>2</sub> (CH<sub>3</sub>CN) under argon. <sup>1</sup>H NMR spectra were recorded on a JEOL LAMBDA-500 (500 MHz) spectrometer, and chemical shifts were quoted in ppm relative to SiMe<sub>4</sub>. All spectra were obtained at room temperature unless otherwise noted. Deuterated solvents were vacuum-transferred from CaH<sub>2</sub> (CD<sub>3</sub>CN) or Na (benzene-d<sub>6</sub>). Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer. The cyclic voltammograms were recorded on an ALS/CHI Model 660 voltammetric analyzer using glassy carbon electrode with Bu<sub>4</sub>NClO<sub>4</sub> as the supporting electrolyte in CH<sub>3</sub>CN. The potential was reported vs. (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe (+0.55 V vs. NHE). The electrospray mass spectra were obtained on a Micromass LCT mass spectrometer. Elemental analyses were performed on a YANACO CHN CORDER MT-6. [(C<sub>5</sub>Me<sub>5</sub>)Co(CO)<sub>2</sub>] and [CoCl(PPh<sub>3</sub>)<sub>3</sub>] were synthesized according to literature procedures [13–15]. The following reagents were used as received: SMe<sub>2</sub>, C<sub>5</sub>Me<sub>5</sub>H, ethylenediamine (en) and 2,2′-bipyridine (bpy) (Tokyo-Kasei Co.); CH<sub>3</sub>NO<sub>2</sub> (Sigma-Aldrich); 1,2-bis(diphenylphosphino)ethane (dppe) and 1,3-bis(diphenylphosphino)propane (dppp) (Kanto-Kagaku Co.).

## 2.2. Crystallography

Crystal data, details of data collection, and refinement parameter for all structurally characterized complexes are summarized in Table 1. Single crystals of (**2**)–(**5**) were obtained by the slow diffusion of Et<sub>2</sub>O to CH<sub>3</sub>CN solutions and (**6**) was obtained from hexane. Crystals were immersed in Paraton-N oil on a nylon loop and transferred to a Mercury CCD diffractometer equipped with Rigaku GNNP low-temperature device. Diffraction data were collected –100 °C under a cold nitrogen stream using graphite monochromated MoK $\alpha$  radiation ( $\lambda$ =0.710690 Å). Equivalent reflections were merged, and the images were processed with the Crystal Clear (Rigaku) program. Corrections for Lorentz-polarization effects and absorption were performed. The structures were solved

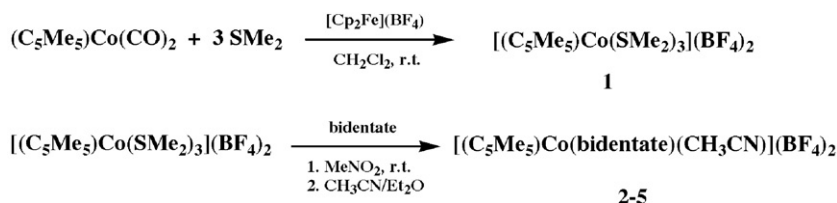
by direct method and refined on *F*<sup>2</sup> by the full-matrix least-square method using Crystal Structure (Rigaku) software package. The hydrogen atoms were put at calculated positions with C–H distances of 0.97 Å. The supplementary crystallographic data are available in CCDC-624423 (**2**), –624424 (**3**), –624425 (**4**), –624426 (**5**), –624427 (**6**).

## 3. Results and discussion

### 3.1. Synthesis of [(C<sub>5</sub>Me<sub>5</sub>)Co(bidentate)(CH<sub>3</sub>CN)](BF<sub>4</sub>)<sub>2</sub> (**2**)–(**5**)

The readily accessible pentamethylcyclopentadienyl complex [(C<sub>5</sub>Me<sub>5</sub>)Co(SMe<sub>2</sub>)<sub>3</sub>](BF<sub>4</sub>)<sub>2</sub> (**1**) was utilized for the synthesis of a series of mononuclear Co(III) complexes. The strong coordination of a pentamethylcyclopentadienyl auxiliary ligand gives the complexes stability during redox changes and high solubility in organic solvents. It is also known that its steric bulkiness often avoids complexity arising from a cluster formation [16,17].

Synthesis of (**1**) was performed on the basis of the Kuhn's method which was described for (C<sub>5</sub>H<sub>5</sub>)Co analogues [18]. The compound (**1**) was obtained as brown powder which could be stored in the glovebox for a prolonged period. Because of instability of (**1**) against moisture, it should be handled under anaerobic conditions for the following ligand substitution reactions.



Scheme 1.

Table 2  
Types of bidentates and yields of  $[(C_5Me_5)Co(bidentate)(CH_3CN)](BF_4)_2$

| Entry | Bidentate | Crystal color | Yield(%) |
|-------|-----------|---------------|----------|
| 2     |           | Orange        | 83       |
| 3     |           | Orange        | 79       |
| 4     |           | Red           | 83       |
| 5     |           | Red           | 46       |

Addition of the bidentate ligands (dppe, dppp, bpy, en) to the  $CH_3NO_2$  solution of (1) resulted in the introduction of the ligands to the  $(C_5Me_5)Co(III)$  fragment. Removal of volatile  $SMe_2$  under reduced pressure facilitated the reaction to complete. Recrystallization from  $CH_3CN/Et_2O$  gave to (2)–(5) in good yields. In analogy with Kuhn's results, we assume that two molecules of  $SMe_2$  on (1) would be substituted by the bidentate ligand, and then the remaining  $SMe_2$  was exchanged to  $CH_3CN$  during recrystallization from  $CH_3CN$  (Scheme 1 and Table 2).

### 3.2. Synthesis of $[(C_5Me_5)Co(dppe)]$ (6)

Kirchner reported the synthesis of (6) utilizing photoirradiation of  $(C_5Me_5)Co(CO)_2$  in the presence of dppe [19]. However, we had difficulty in repeating this synthesis. Therefore, we decided to use  $ClCo(PPh_3)_3$  as a starting material. Although Song et al. reported introduction of cyclopentadienyl derivatives ( $C_5H_4-R$ ;  $R=CO_2Et$ ,  $COMe$ ) to obtain  $(C_5H_4-R)Co(PPh_3)_2$  by reactions of  $ClCo(PPh_3)_3$  and  $NaC_5H_4R$  in benzene/THF, synthesis of  $C_5Me_5$  analogue in this method was not described [20]. Thus, at first, we tried to isolate  $(C_5Me_5)Co(PPh_3)_2$  by the reaction of  $ClCo(PPh_3)_3$  with  $Li(C_5Me_5)$ , but the obtained material from this reaction was a dimer compound and no  $(C_5Me_5)Co(PPh_3)_2$  was isolated. The property and structure of this resulting dimer compound will be reported elsewhere. With this result, as the second trial, we chose to introduce dppe to the starting material. A reaction of  $PPh_3$ , dppe and  $CoCl_2 \cdot 6H_2O$  (1:1:1) followed by treatment with  $NaBH_4$  gave a green powder, which is expected to contain  $ClCo(PPh_3)(dppe)$ . The reaction of this green powder with  $Li(C_5Me_5)$  resulted in a formation of red crystals of (6) in 21% yield (Scheme 2).

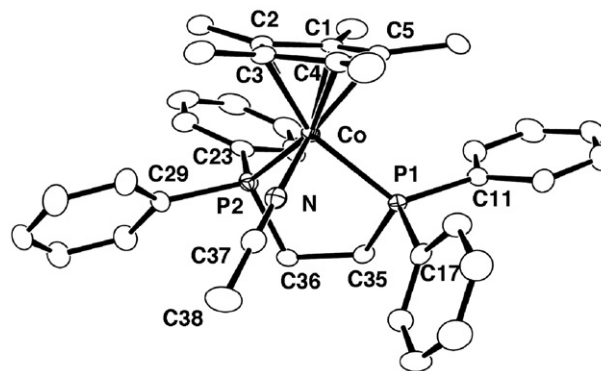


Fig. 1. Structure of the cationic part of (2).

### 3.3. Structures

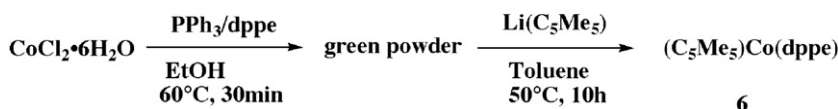
X-ray crystallographic analysis was performed for (2)–(5) and (6). The molecular structure of the cation part of (2) is shown in Fig. 1, and the structure of (6) is given in Fig. 2. Table 3 lists the selected bond distances and bond angles for (2) and (6). The divalent cationic part of (2) adopts a typical octahedral arrangement at Co with one  $C_5Me_5$  ring, two phosphines and one  $CH_3CN$ . Compound (6) possesses a distorted trigonal bipyramidal coordination geometry, where C(2) and P(2) occupy the axial positions with C(2)–Co–P(2) angle  $171.8^\circ$  and P(1) and centers of C(3)–C(4) and C(1)–C(5) make up the triangle base. The P–Co–P angles in (2) and (6) do not differ much ( $87.67^\circ$  for compound (2) and  $87.30^\circ$  for compound (6)), while the average length of Co–P bond is different. Despite the highly cationic property of (2), the average bond length of (2) ( $2.264 \text{ \AA}$ ) is longer than that of (6) ( $2.109 \text{ \AA}$ ) and it is suggested that a  $d\pi-p\pi$  interaction between electron-rich Co(I) center and aryl-phosphine ligand. Further, lower coordination numbers give shorter bond length in general.

The different coordination numbers of these complexes can be attributed to the 18 electron rule. The Co(III) complex (2) is 18-electron, whereas the Co(I) complex (6) has two more electrons but one less ligand ( $CH_3CN$ ), resulting in the same 18-electron.

### 3.4. Voltammetry

Cyclic voltammograms were measured for compounds (2)–(5) and the half-wave potentials are listed in Table 4.

Each complex exhibits two one-electron reductions that are chemically reversible in  $CH_3CN$  solutions. The first reductions appearing from  $-0.56$  to  $-0.98 \text{ V}$  (vs.  $CP_2Fe/CP_2Fe^+$ ) are assignable to Co(III)/Co(II) process and the second reductions, being over  $-1.13 \text{ V}$ , are assignable to Co(II)/Co(I) process. No decrease of peak currents for each redox wave was observed



Scheme 2.

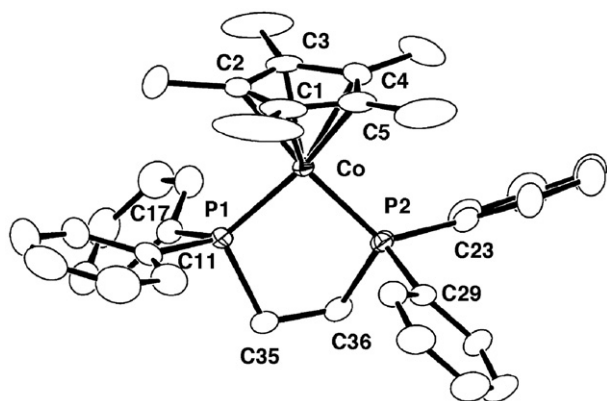


Fig. 2. Molecular structure of (6).

during multiple sweeps. Interestingly, half-wave potentials for Co(II)/Co(I) process of (5) was much lower than those for (2)–(4). Such difference is reasonable, because dppe, dppp and bpy can relax the high electron density on the Co(I) center by accepting d electron to the  $\pi^*$  orbitals in the process of Co(II)/Co(I) whereas ethylenediamine (en) cannot accept electron because it does not have  $\pi^*$  orbitals. A cyclic voltammogram of the Co(I) complex (6) was also measured in  $\text{CH}_3\text{CN}$  solution and two chemically reversible one-electron oxidations were observed. The half-wave potentials were very close to those of (2) though the sweeping directions were opposite. These results

Table 3  
Selected bond distances (Å) and angles ( $^\circ$ ) for  $[(\text{C}_5\text{Me}_5)\text{Co}(\text{dppe})(\text{CH}_3\text{CN})](\text{BF}_4)_2$  (2) and  $(\text{C}_5\text{Me}_5)\text{Co}(\text{dppe})$  (6)

| $[(\text{C}_5\text{Me}_5)\text{Co}(\text{dppe})(\text{CH}_3\text{CN})](\text{BF}_4)_2$ (2) |             |            |             |
|--|-------------|------------|-------------|
| <i>Bond length</i>   |             |            |             |
| Co–P1  | 2.2733 (10) | P1–C11     | 1.824 (3)   |
| Co–P2  | 2.2550 (10) | P1–C35     | 1.838 (3)   |
| Co–N   | 1.913 (3)   | P2–C23     | 1.828 (3)   |
| Co–C1  | 2.071 (3)   | P2–C36     | 1.835 (3)   |
| Co–C2  | 2.120 (3)   | C35–C36    | 1.526 (5)   |
| Co–C3  | 2.127 (3)   | C37–N      | 1.146 (4)   |
| Co–C4  | 2.119 (3)   | C37–C38    | 1.454 (5)   |
| Co–C5  | 2.129 (3)   |            |             |
| <i>Angles</i>  |             |            |             |
| P1–Co–P2   | 87.69 (3)   | C11–P1–C17 | 106.52 (16) |
| P1–Co–N  | 88.09 (9)   | C23–P2–C29 | 103.33 (17) |
| P2–Co–N  | 88.34 (1)   | P1–C35–C36 | 112.0 (2)   |
| C1–Co–C5   | 39.88 (14)  | P2–C36–C35 | 111.8 (2)   |
| Co–N–C37   | 175.8 (3)   | N–C37–C38  | 177.6 (4)   |
| $(\text{C}_5\text{Me}_5)\text{Co}(\text{dppe})$ (6)  |             |            |             |
| <i>Bond length</i>   |             |            |             |
| Co–P1  | 2.1093 (7)  | Co–C4      | 2.090 (3)   |
| Co–P2  | 2.1077 (7)  | Co–C5      | 2.072 (3)   |
| Co–C1  | 2.094 (3)   | P1–C35     | 1.858 (3)   |
| Co–C2  | 2.072 (3)   | C35–C36    | 1.530 (4)   |
| Co–C3  | 2.112 (3)   |            |             |
| <i>Angles</i>  |             |            |             |
| P1–Co–P2   | 87.30 (3)   | C11–P1–C17 | 102.2 (1)   |
| C1–Co–C2   | 39.8 (2)    | P1–C35–C36 | 105.3 (2)   |

Table 4  
Cyclic voltammetric data of the compounds (2)–(6)

| Entry | Bidentate | $E_{1/2}$ (V vs. $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ ) |              |
|-------|-----------|--|--------------|
|       |           | Co(III)/Co(II)   | Co(II)/Co(I) |
| 2     |           | −0.61  | −1.13        |
| 3     |           | −0.56  | −1.26        |
| 4     |           | −0.82  | −1.15        |
| 5     |           | −0.98  | −2.25        |
| 6     |           | −0.57  | −1.12        |

Conditions:  $4.00 \times 10^{-3}$  M in  $\text{CH}_3\text{CN}$ , 0.10 M  $n\text{Bu}_4\text{NClO}_4$ , highly polished glassy carbon working electrode (scan rate  $0.100 \text{ Vs}^{-1}$ ).

suggest that, in these complexes, the two-electron redox process is accompanied by a reversible change between five-coordinated and six-coordinated structures, which comes from release and coordination of a  $\text{CH}_3\text{CN}$  molecule. During this process the structural motif “ $(\text{C}_5\text{Me}_5)\text{Co}(\text{dppe})$ ” is retained intact. Such durability against a variation of oxidation states will be essential to a catalytic activity involving electron donation to a substrate, such as reduction of  $\text{H}^+$  to  $\text{H}_2$ .

As further investigation of this functionality, a cyclic voltammogram of (2) was measured in the presence of p-toluenesulfonic acid. Fig. 3 shows the cyclic voltammogram of (2) before (solid line) and after (dotted line) an addition of the acid. After the addition of acid, the oxidation wave from Co(I)

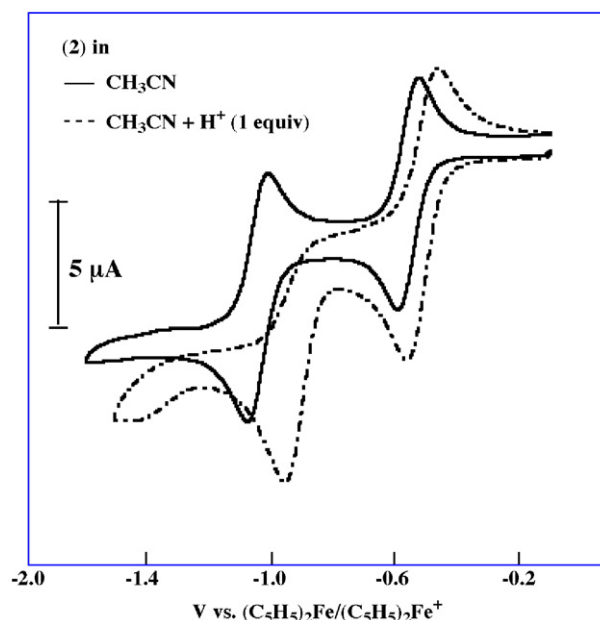


Fig. 3. Cyclic voltammograms of (2).



to Co(II) disappeared and while the oxidation wave from Co(II) to Co(III) remained unchanged. The reduction wave from Co(II) to Co(I) showed a positive shift, which suggests that the Co(I) species reacted with  $H^+$  to give a Co–H complex [21]. This Co–H species was then converted to Co(II) with concurrent formation of  $H_2$ . There are two possible mechanisms for this step; one is that two molecules of the Co–H complex produce two Co(II) molecules and one molecule of  $H_2$ , and the other is that the Co–H species abstracts a hydrogen atom ( $H\cdot$ ) from the surrounding medium (the solvent or the supporting electrolyte). We prefer the former mechanism, because in the latter case, a 19-electron, seven-coordinated Co species “(C<sub>5</sub>Me<sub>5</sub>)CoH<sub>2</sub>(dppe)” must be present as an intermediate, which is highly unlikely. We attempted the bulk electrolysis to detect  $H_2$ , but it was not successful because of the limited stability of the Co(I) species under these conditions. Trials to characterize the intermediates and to detect  $H_2$  are currently under way.

#### 4. Conclusion

An efficient synthesis of [(C<sub>5</sub>Me<sub>5</sub>)Co(bidentate)(CH<sub>3</sub>CN)](BF<sub>4</sub>)<sub>2</sub> is reported. By using SMe<sub>2</sub> ligand in the starting material, several bidentate ligands were cleanly introduced to the (C<sub>5</sub>Me<sub>5</sub>)Co core to form a series of six-coordinated Co(III) complexes. The Co(I) five coordinated complex having similar components (C<sub>5</sub>Me<sub>5</sub> and dppe) was synthesized. These Co complexes are electrochemically interconvertible between Co(III) and Co(I) in CH<sub>3</sub>CN solutions with structural transformation. The durability of “(C<sub>5</sub>Me<sub>5</sub>)Co(dppe)” motif should be advantageous for catalytic reduction. Further investigation of the reduction of  $H^+$  to  $H_2$  by using these Co complexes is now in progress.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.bbabo.2006.12.005.

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